Structural forms of cubic BC$_2$N

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Superhard cubic boron-carbonitrides (c-BC$_2$N) are studied with the use of the *ab initio* pseudopotential density functional method. The total energy, lattice constant, bulk and shear moduli, and electronic band structures as well as the electron density of states are calculated for all the possible c-BC$_2$N structures in an eight-atom zinc-blende-structured cubic unit cell. The results obtained provide a plausible explanation for recent experimental observations as well as a possible path to synthesis of the materials.

I. INTRODUCTION

Searching for new superhard materials with better performance properties under extreme conditions, such as high pressure and temperature, is an important experimental and theoretical research field. Similarities between diamond and cubic boron nitride (c-BN), such as their closely matched lattices, high melting temperatures, large bulk moduli, high thermal coefficients, and similar thermal-expansion coefficients, motivate the expectation that zinc-blende-structured cubic boron-carbonitride (c-BCN) compounds may form new superhard and superabrasive materials.

Recently, several successful syntheses of c-BCN compounds have been reported in the literature. Nakano *et al.*[1] reported the direct transformation under high pressure (7.7 GPa) and high temperature (∼2000–2400 K) from graphitic BC$_2$N (g-BC$_2$N) to c-BCN compounds, which tend to segregate into diamond and c-BN-like structures at higher temperature. Knittle *et al.*[2] prepared a c-BC$_x$N ($x=0.9$–3.0) solid solution using even higher static pressure (30 GPa) and laser heating (∼2000–2500 K), starting from either the microcrystalline BCN, or the mechanical mixture of graphitic carbon and boron nitride. The c-BCN solid solution was found to have a bulk modulus (355 GPa) slightly lower than that of c-BN, with a lattice constant 0.3% larger than that predicted based on the ideal mixing of diamond and c-BN. Komatsu *et al.*[3] attempted to synthesis c-BC$_{2.5}$N from g-BC$_{2.5}$N using shock-wave compression and obtained a higher bulk modulus (401 GPa), with a lattice constant 0.5% larger than that predicted based on ideal mixing. Very recently, Solozhenko *et al.*[4] synthesized c-BC$_2$N from g-BC$_2$N using high pressure (25.8 GPa) and laser heating. When the temperature is higher than 2200 K, they claimed to obtain a c-BC$_2$N structure with a low bulk modulus (282 GPa), large lattice constant (1.4% larger than that of ideal mixing) and very high hardness. The Vickers (Knoop) hardness of the c-BC$_2$N obtained is 76 GPa (55 GPa) compared with those of 115 GPa (63 GPa) for diamond and 62 GPa (45 GPa) for c-BN. The diverse experimental results mentioned above may result from the fact that the c-BCN compounds synthesized in these experiments belong to different metastable structures of the material.

Several first-principles studies on the structure of the c-BCN compounds have been reported.[5–8] To reduce the number of different test structures, models with lower energy are constructed by avoiding B-B and N-N bonds and separating the BN layer from the carbon layer in the unit cell. This results in only a few of the possible structures of the c-BCN compounds being studied. As mentioned above, experimental results seem to indicate the possibility of producing different structures of the c-BCN compounds. It is instructive to compare the total energy difference (per atom) between "all" the possible structures within the thermal energy $k_B T$ ($T \sim 2000$–3000 K) during the synthesis processes. Despite the diversity which appears in the experimentally obtained lattice constants and bulk moduli, the synthesized c-BC$_2$N all show a very weak or the absence of the (002) x-ray diffraction line. Two possible structures of c-BC$_2$N are consistent with the absence of the (002) x-ray diffraction lines: one possibility is that B, C, and N atoms are randomly distributed over the zinc-blende-structure lattice, and the other is that B and N atoms distribute randomly over one fcc sublattice, with C atoms on the other. It is interesting to know which structure is more likely to appear in the synthesis process.

In this paper, *ab initio* pseudopotential local-density-functional (LDA) calculations are carried out for the c-BC$_2$N which has been most frequently prepared in the experiments. All possible structures in an eight-atom zinc-blende-structured cubic unit cell are studied. Fortunately, out of 420 different configurations only seven are topologically different, due to the high symmetry of the zinc-blende-structured lattice, which makes our study possible. The calculated total energy, structural parameters, bulk and shear moduli, and electronic band structures as well as electron density of states should aid in understanding and analyzing the experimental results obtained and give estimations of the potential of c-BC$_2$N as a superhard material.

II. METHOD OF CALCULATION AND STRUCTURAL MODEL

The total energy of c-BC$_2$N is computed as a function of strain using the LDA pseudopotential total-energy scheme with a plane-wave basis set.[9–11] The energy of the structures

TABLE I. Comparison with experiments.

Structure		Diamond	c-BN
Lattice constant			
a_0 (Å)	This work	3.539	3.594
	Expt.	3.567[a]	3.617[b]
Bulk moduli			
B_0 (GPa)	This work	457.4	393.2
	Expt.	443[a]	368[b]
Shear moduli			
C_{44} (GPa)	This work	599.4	471.7
	Expt.	576[c]	480[d]
$(C_{11}-C_{12})/2$ (GPa)	This work	468.5	310.5
	Expt.	475[c]	315[d]
Total energy			
$-E$(eV/atom)	This work	155.501	175.673

[a]Reference 13.
[b]Reference 2.
[c]Reference 14.
[d]Reference 15.

is minimized by relaxing the structural parameters using a quasi-Newton method.[12] Comparison of the calculated and measured results for diamond and c-BN are listed in Table I. The agreement is satisfactory, with errors of less than 1% in the lattice constant and 5% in bulk and shear moduli.

The bulk moduli of the c-BC$_2$N structures are obtained by calculating the total energy of each structure as a function of the volume of its unit cell. The structure is fully relaxed at each volume and then the results are fit to the Birch-Murnaghan equation of state. The average shear moduli of the c-BC$_2$N structures are obtained by calculating the stresses of the c-BC$_2$N structures when small strains are applied to each relaxed structure. As the relaxed c-BC$_2$N structures are slightly deformed from cubic, we define the following average shear moduli:

$$\overline{C}_{44} = \tfrac{1}{3}(C_{xy,xy} + C_{yz,yz} + C_{zx,zx}),$$

$$\overline{C_{11}-C_{12}} = \tfrac{1}{3}[(C_{xx,xx} + C_{yy,yy} + C_{zz,zz})$$
$$-(C_{xx,yy} + C_{yy,zz} + C_{zz,xx})]. \quad (1)$$

In Fig. 1, we show all possible topologically different structures (after structural relaxation) for c-BC$_2$N in an eight-atom unit cell. The initial structures are cubic zinc blende. The structures are numbered according to the increasing numbers of B-B and N-N bonds in the structures. Struc-1 is constructed by avoiding B-B and N-N bonds, and separating the BN layers from C layers. Similarly, struc-2 is also B-B and N-N bonds free, but with B, N, and C atoms mixed in the same layers. In struc-3, B and N atoms occupy one fcc sublattice, while C atoms occupy another. Struc-4 and struc-5 have one B-B bond and one N-N bond, respectively. And struc-6 and struc-7 both have B-B and N-N bonds. The number of topologically equivalent configurations corresponding to each structure in Fig. 1 are listed in the last row in Table II, which sums up to the total of
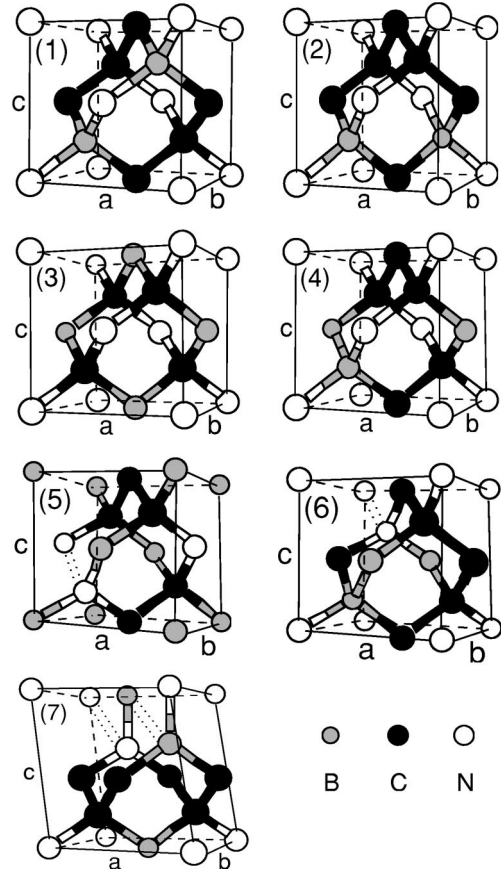

FIG. 1. All the possible topologically different c-BC$_2$N structures (after structural relaxation) starting from an eight-atom zinc-blende-structured unit cell. The dotted bonds indicate the broken covalent bonds between N atoms.

$8!/(2!)^2 4! = 420$ possible configuration structures in the eight-atom zinc-blende-structured cubic BC$_2$N unit cell.

III. RESULTS AND DISCUSSION

The calculated structures of the seven c-BC$_2$N shown in Fig. 1 are listed in Table II together with the calculated total energy E, the average lattice constance $\overline{a}$ defined as the cubic root of the volume of the unit cell, the bulk modulus B_0, the average shear moduli $\overline{C}_{44}$ and $(\overline{C_{11}-C_{12}})/2$, and the number and length of different bonds in the unit cell, as well as the number of topologically equivalent configurations of each structure. The available experimental results are also given in Table II for comparison.

Among the seven structures studied in Fig. 1, struc-1 and struc-2 have the lowest energies. But all the c-BC$_2$N structures have positive formation energy, defined as $E_f = E_{BC_2N} - (E_{diamond} + E_{c-BN})/2$, which indicates that c-BC$_2$N structures are metastable structures and tend to separate into diamond and c-BN phase structures. Struc-1 was expected to be a low-energy structure in several previous *ab initio* calculations[5,7,8] because of the separation of the BN and C layers and the lack of N-N and B-B bonds in the structure. Our results show that N-N and B-B bonds do increase the

TABLE II. Structural parameters for c-BC_2N.

Structure	1	2	3	4	5	6	7	Expt.
a(Å)	3.570	3.568	3.584	3.592	3.643	3.655	3.591	
b(Å)	3.609	3.564	3.634	3.597	3.689	3.655	3.591	
c(Å)	3.570	3.613	3.584	3.592	3.643	3.665	3.591	
α(°)	89.50	90.00	90.00	89.82	87.27	87.10	78.37	
β(°)	90.00	90.00	90.00	90.38	93.06	87.10	101.6	
γ(°)	90.00	90.00	90.00	90.18	92.73	87.11	90.19	
$\bar{a}$ (Å)	3.583	3.582	3.601	3.594	3.654	3.654	3.715	3.602,[a] 3.642[b]
E(eV/atom)	-165.09	-165.08	-164.64	-164.75	-164.82	-164.72	-164.96	
B_0 (GPa)	399.7	400.1	369.9	379.6	291.5	295.9	309.7	355,[a] 282[b]
$\overline{C_{44}}$ (GPa)	484.2	493.0	456.3	454.9	392.1	385.5	315.3	
$\overline{(C_{11}-C_{12})}/2$ (GPa)	352.4	314.3	366.3	367.7	257.9	254.7	257.4	
No. C-C bond	4	4	0	3	3	4	4	
No. B-N bond	4	4	0	2	2	2	2	
No. C-N bond	4	4	8	6	4	4	4	
No. C-B bond	4	4	8	4	6	4	4	
No. B-B bond	0	0	0	1	0	1	1	
No. N-N bond	0	0	0	0	1	1	1	
C-C length (Å)	1.514	1.526		1.514	1.558	1.559	1.553	
				1.575	1.650	1.594	1.576	
						1.651		
B-N length (Å)	1.562	1.575		1.562	1.464	1.466	1.414	
C-N length (Å)	1.555	1.540	1.551	1.555	1.420	1.425	1.451	
				1.562	1.431	1.435		
C-B length (Å)	1.575	1.563	1.567	1.514	1.584	1.582	1.581	
				1.575	1.606	1.710		
					1.732			
B-B length (Å)				1.575		1.639	2.720	
N-N length (Å)					2.196	2.202	2.969	
No. equiv. conf.	24	48	12	96	96	96	48	

[a]Reference 2.
[b]Reference 4.

total energy of the c-BC_2N structures, but the mixing of B, N, and C atoms does not necessarily increase the total energy. The energy of struc-2 is almost as low as struc-1. The results listed in Table II are consistent with previous *ab initio* calculations for struc-1,[7,8] but contradictory to a recent density functional based tight-binding calculation[16] which predicted a lower energy (and negative formation energy) for struc-3 than that of struc-1. Our results show that struc-3 has the highest total energy among the seven structures in Fig. 1, even though it has no B-B or N-N bonds.

It is interesting to compare struc-4 and struc-5 in Fig. 1, which have, respectively, a B-B bond and an N-N bond before the structural relaxation. After relaxation, the length of the N-N pair in struc-5 becomes 2.1957 Å, much longer than that (1.5745 Å) of the B-B pair in struc-4. The covalent bond between the N-N pair (indicated as the dotted bond in Fig. 1) has been broken, which increases the volume (or $\bar{a}$) of the unit cell and decreases the bulk and shear moduli of struc-5. Struc-4 retains a covalent B-B bond, and thus has a high bulk and shear modulus, although the B-B bond increases its total energy just as the N-N bond does in struc-5.

The N-N and B-B pairs in struc-6 behave similarly as those in struc-4 and struc-5, with the former repelling each other to break the covalent bond (the dotted bond in Fig. 1), while the latter remains covalent. The volume (or $\bar{a}$) of the unit cell and the bulk and shear moduli of struc-6 are almost exactly the same as those of struc-5. Struc-7 is distorted greatly from its original structure after structural relaxation. As the N-N and B-B pairs are parallel to each other, both expand and break their covalent bonds, giving rise to a structure where all C atoms have sp^3 bonds, while N and B atoms have sp^2 bonds. Struc-7 has the largest volume for the unit cell and a lower energy compared to those of struc-3–6. However, the relaxed structure of struc-7 is far from the cubic structure.

It is well known that the LDA systematically predicts somewhat smaller lattice constants than are found experimentally (see Table I). Taking this into account, we believe that the most probable structure of the c-BC_2N solid solution prepared by Knittle *et al.*[2] is struc-1 or struc-2, or a mixture of both. The lower bulk modulus observed in the experiment compared to our calculated results (see Table II) can also be partly attributed to the fact that LDA calculations give
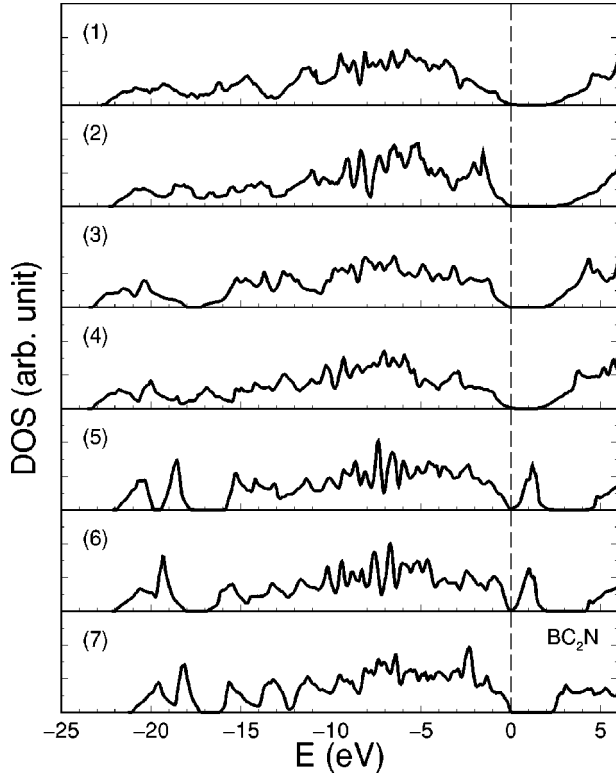
FIG. 2. The total electronic density of states of the seven c-BC_2N structures in Fig. 1.

smaller lattice constants. Since the bulk moduli of the tetrahedrally bounded materials are well described by the empirical formula[17] $B_0 \propto d^{7/2} \propto \bar{a}^{7/2}$ where d is the bond length, a 1% reduction in $\bar{a}$ will give about a 4% increase in B_0. So the estimated bulk moduli of struc-1 and struc-2 are about 380 GPa, which is still slightly higher than that observed in the

experiment. This discrepancy may be due to the incomplete transformation of g-BC_2N to c-BC_2N in the experiment, indicated by the presence of a weak (002) x-ray diffraction line of the sample,[2] which is the strongest diffraction line of the g-BC_2N. The layer structured g-BC_2N gives rise to a low bulk modulus. The calculated bulk and shear moduli in Table II suggest that struc-1 and struc-2 are the hardest structures among the seven structures shown in Fig. 1.

Very recently, a low-density c-BC_2N structure was synthesized by Solozhenko *et al.*[4] which has a large lattice constant ($a_0 = 3.642$ Å) and low bulk modulus ($B_0 = 282$ GPa). The sample appears to exhibit extreme hardness, slightly less than that of diamond. Based on the fact that the (002) x-ray diffraction line of the sample is absent, it was suggested by the authors that the structure of this low-density c-BC_2N is either a zinc-blende-structured lattice with B, C, and N atoms randomly distributed on the lattice or with B and N atoms distributed randomly on one fcc sublattice and C atoms on the other. Our results (Table II) show that the latter structure (struc-3) has a smaller lattice constant than measured and much too high a bulk modulus compared with the experimental results, while struc-5 and struc-6 have lattice constants and bulk modulus close to the experimental results. We believe that a possible structure of the low-density c-BC_2N synthesized by Solozhenko *et al.*[4] is a (deformed) zinc-blende-structured lattice where B, C, and N atoms are randomly distributed with significant N atoms forming N-N pairs, as in struc-5 and struc-6 in Fig. 1. The N atoms in the N-N pair repel each other to break the covalent bond, which results in a large lattice constant and low bulk modulus of this low-density c-BC_2N phase. Our calculated results also show that struc-5 and struc-6 have both lower bulk and shear moduli comparing with those of c-BN. It seems questionable that this low-density c-BC_2N structure is harder than c-BN, as predicted by Solozhenko *et al.*[4] Also, it appears that the
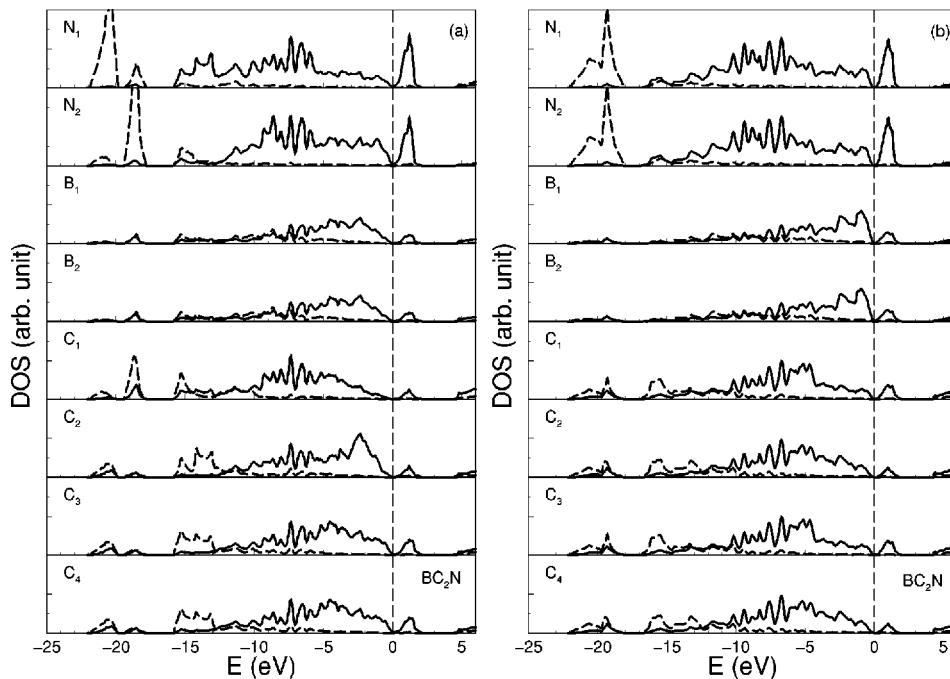

FIG. 3. The s (solid lines) and p (dashed lines) local density of states of atoms in (a) struc-5 and (b) struc-6 shown in Fig. 1.
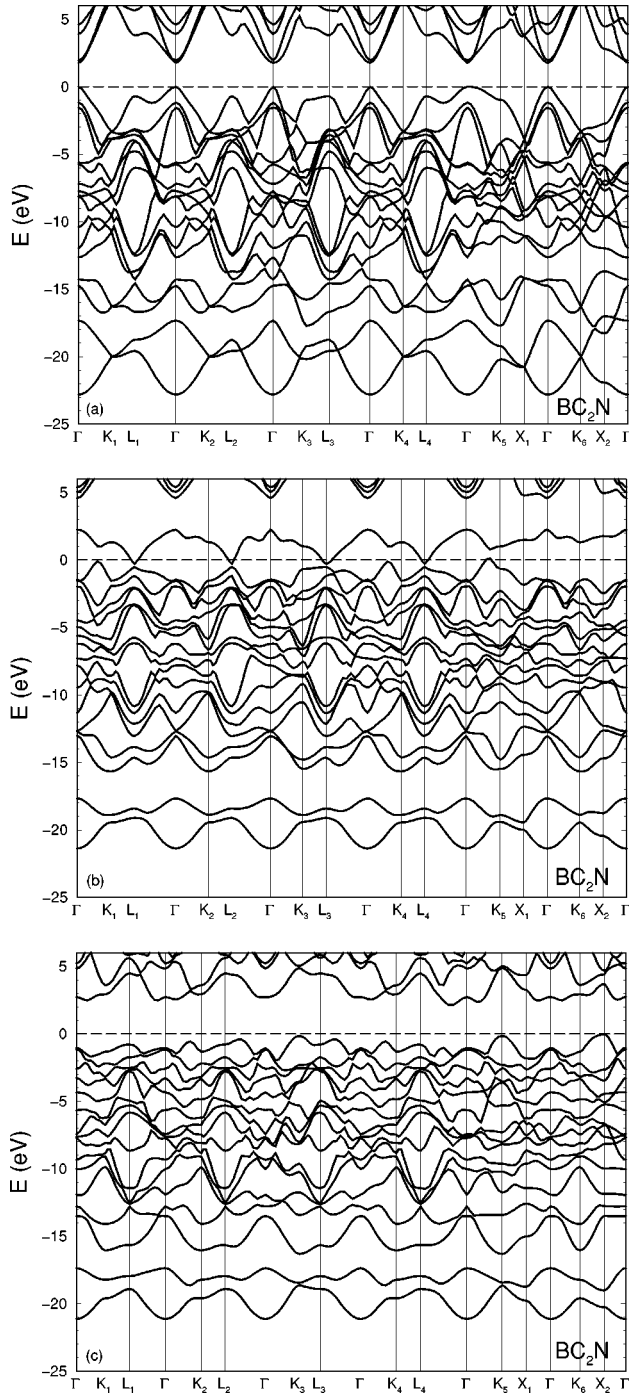
FIG. 4. The electronic band structures of the c-BC$_2$N structures of (a) struc-1, (b) struc-5, and (c) struc-7 shown in Fig. 1. The k points labeled on the horizontal axes are defined in Fig. 5.
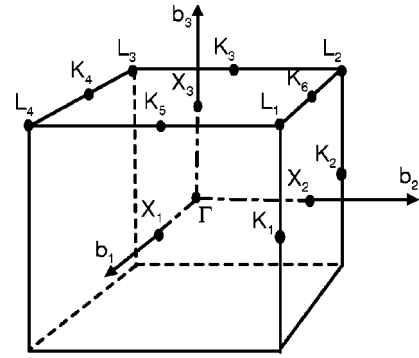

FIG. 5. Definition of the k points in the reciprocal lattice used in the calculation of the energy band structures in Fig. 4.

haps, it is not by accident that each synthesized c-BC$_2$N structure reported in the literature corresponds to two closely resembled structures in Table II (struc-1,2 and struc-5,6).

In Fig. 2, we plot the electronic density of states for the seven c-BC$_2$N structures shown in Fig. 1, where the top valence band is set at $E=0$. The calculated energy gaps of struc-1 and struc-2 are about 2 eV. As the LDA tends to underestimate the energy gap by 65–75 % for c-BN and diamond, an energy gap of 3 eV is estimated for the c-BC$_2$N synthesized by Knittle *et al.*[2] Zero-energy gaps are predicted for struc-5 and struc-6. In Fig. 3, we plot the s (the dashed lines) and p (the solid lines) local density of states of each atom in the unit cell in struc-5 [Fig. 3(a)] and struc-6 [Fig. 3(b)]. It is obvious that the lowest conduction bands come mainly from the p states of the N atoms in struc-5 and struc-6. As the LDA does not give correct energy gaps, especially for narrow-gap structures, we are not sure if struc-5 and struc-6 are metals or semiconductors. However, even if they are semiconductors, their band gaps will be much smaller than those of struc-1 and struc-2. This suggests that electronic and optical measurements can be used to help identify our analysis of the structural forms of c-BC$_2$N.

The electronic band structures of the c-BC$_2$N structures are plotted in Fig. 4 for (a) struc-1, (b) struc-5, and (c) struc-7. The band structures of struc-2–4 are similar to that of struc-1, and the band structure of struc-6 is similar to that of struc-5. The k points labeled on the horizontal axes in Fig. 4 are defined in Fig. 5. The energy bands are calculated along the straight lines between any of the two neighboring k points. As the relaxed structures of c-BC$_2$N in Fig. 1 are not exactly cubic, energy bands are calculated between as many k points as possible. Within the LDA, struc-1–4 are semiconductors with direct band gaps of 1.9, 2.1, 1.9, and 0.9 eV, respectively. Struc-5,6 are predicated by the LDA as semimetals. Struc-7 is semiconducting with an indirect band gap of 2.1 eV. Similar metallic electronic band structures were also predicted by the LDA for some g-BC$_2$N structures.[18] As we commented on before, this prediction using the LDA is not 100% reliable, especially when the conduction and valence bands overlap only slightly as in Fig. 4(b). More sophisticated methods, such as the *ab initio* pseudopotential GW approach,[19] need to be applied to determine whether these structures are metals or semiconductors with narrow band gaps.

sample used by Solozhenko *et al.*[4] to measure the hardness was synthesized in a very different manner from the one that they used to synthesis the low-density c-BC$_2$N to measure the lattice constant and bulk modulus. The energy difference between struc-1 and struc-5 is 266 meV/atom, which is about the same order of magnitude as the thermal energy, 172 meV ($T=2000$ K) at which or above which the c-BC$_2$N samples were synthesized. Most of the structures in Fig. 1 can be created under high pressure and at high temperatures. Per-

IV. CONCLUSION

The structural form of c-BC$_2$N is studied with the *ab initio* pseudopotential density functional method for all the possible c-BC$_2$N structures starting from an eight-atom zinc-blende-structured cubic unit cell. The c-BC$_2$N structures are expected to be metastable. The hardest structures of c-BC$_2$N studied have bulk and shear moduli comparable to or slightly higher than those of c-BN, which we believe is similar to c-BC$_2$N synthesized by Knittle *et al.*[2] A (deformed) zinc-blende-structured lattice where B, C, and N atoms are randomly distributed with significant N atoms forming N-N pairs is suggested as a possible structure for the low-density c-BC$_2$N phase synthesized very recently by Solozhenko *et al.*[4] The broken covalent bond in the N-N pair is responsible for the low bulk modulus and large lattice constant for this c-BC$_2$N phase as observed in the experiment. Contradictory to the experimental prediction that the hardness of this c-BC$_2$N structure is only slightly below diamond, the bulk and shear moduli we calculated indicate that the structure should be softer than c-BN. The calculated electronic band structures and electron density of states of the c-BC$_2$N structures suggest that the low-density c-BC$_2$N phase synthesized by Solozhenko *et al.*[4] has very different electronic band structures compared to the c-BC$_2$N structure synthesized by Knittle *et al.*[2] Further electronic and optical measurements are encouraged to aid in the analyses of the c-BC$_2$N structures.

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